Science of the Total Environment 538 (2015) 431–444

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Trends in pesticide concentrations and use for major rivers of the United States

Karen R. Ryberg [a,*], Robert J. Gilliom [b]

[a] U.S. Geological Survey (USGS), 821 E Interstate Avenue, Bismarck, ND 58503, USA
[b] USGS, 6000 J Street, Placer Hall, Sacramento, CA 95819, USA

HIGHLIGHTS

- Concentration and use trends were assessed for 11 pesticides in 38 US rivers.
- Concentration and use trends mostly agreed for agricultural pesticides.
- Regulations and urban-stream trends explain trends related to nonagricultural use.
- For most trend discrepancies, concentration increased more than use.
- Unaccounted use may contribute to greater concentration increases in some cases.

ARTICLE INFO

Article history:
Received 1 May 2015
Received in revised form 23 June 2015
Accepted 23 June 2015
Available online xxxx

Editor: D. Barcelo

Keywords:
Pesticides
Trends
Pesticide use
Surface water
Water quality
Rivers

ABSTRACT

Trends in pesticide concentrations in 38 major rivers of the United States were evaluated in relation to use trends for 11 commonly occurring pesticide compounds. Pesticides monitored in water were analyzed for trends in concentration in three overlapping periods, 1992–2001, 1997–2006, and 2001–2010 to facilitate comparisons among sites with variable sample distributions over time and among pesticides with changes in use during different periods and durations. Concentration trends were analyzed using the SEAWAVE-Q model, which incorporates intra-annual variability in concentration and measures of long-term, mid-term, and short-term streamflow variability. Trends in agricultural use within each of the river basins were determined using interval-censored regression with high and low estimates of use.

Pesticides strongly dominated by agricultural use (cyanazine, alachlor, atrazine and its degradate deethylatrazine, metolachlor, and carbofuran) had widespread agreement between concentration trends and use trends. Pesticides with substantial use in both agricultural and nonagricultural applications (simazine, chlorpyrifos, malathion, diazinon, and carbaryl) had concentration trends that were mostly explained by a combination of agricultural-use trends, regulatory changes, and urban use changes inferred from concentration trends in urban streams. When there were differences, concentration trends usually were greater than use trends (increased more or decreased less). These differences may occur because of such factors as unaccounted pesticide uses, delayed transport to the river through groundwater, greater uncertainty in the use data, or unquantified land use and management practice changes.

Published by Elsevier B.V.

1. Introduction

The use of pesticides has a range of benefits, including increased food production and reduction of insect-borne diseases, but also raises concerns about possible adverse effects on the environment, including water quality. Once released into the environment, pesticides can move through the hydrologic system to streams and groundwater, where they may have unintended effects on humans, aquatic life, or wildlife. Understanding the long-term trends of pesticide concentrations in the hydrologic system is essential to understanding their potential for adverse effects, how past use has affected concentrations in streams and rivers, and how future changes in use or management may affect concentration trends.

Previous analyses of concentration trends in rivers and streams of the United States (US) Corn Belt showed that trends in major rivers and their tributaries were largely consistent with each other and with use trends, and that the concentration trends in large rivers provide a smoothed indication of large scale trends (Sullivan et al., 2009; Vecchia et al., 2009). Use data generally are not available for estimation of nonagricultural uses of pesticides, but an analysis of concentration trends in urban streams showed varying patterns in trend direction

* Corresponding author.

http://dx.doi.org/10.1016/j.scitotenv.2015.06.095
0048-9697/Published by Elsevier B.V.

depending on analysis period, region of the US, chemical, and regulatory actions (Ryberg et al., 2010). Stone et al. (2014) summarized trends for a subset of pesticides used in agricultural and urban settings over the last two decades (1992–2011) and reported widespread trends in pesticide concentrations in surface water that varied in direction in response to changes in use driven by regulatory actions and new pesticide introductions.

This paper presents an analysis of trends in pesticide concentrations and agricultural-use intensity (agricultural use) for 11 compounds in 38 major rivers of the US (Fig. 1, Table 1), a subset of the trend analysis of Ryberg et al. (2014). The pesticides include the herbicides cyanazine, alachlor, atrazine and its degradate deethylatrazine (DEA), metolachlor, and simazine; and the insecticides chlorpyrifos, malathion, diazinon, carbofuran, and carbaryl. All 11 compounds are among the top 20 most frequently detected in US streams and rivers (based on those analyzed by the U.S. Geological Survey National Water-Quality Assessment Program; Stone et al., 2014). The analysis was limited to pesticides that met the specific data requirements for trend analysis and data deficiencies leave out many important compounds, such as glyphosate, pyrethroids, and neonicotinoids. Glyphosate, for example, is "difficult and costly to measure" and assessment efforts in the US have been "limited primarily to regional, targeted, or short-term studies" (Stone et al., 2014). Supplementary Table 1 contains chemical properties affecting the transport and fate of the compounds.

The analysis of paired concentration and use trends in the present study contributes to a better understanding of how long-term trends in concentration are affected by use and regulatory changes. The compounds included have a wide variety of uses and the major rivers evaluated are distributed across the US. National annual agricultural use estimates for the five herbicides and five insecticides are shown in Fig. 2. The use estimates are shown in terms of the types of crops they are used on and the estimates highlight changes in pesticide use and regulation and changes in national cropping patterns. Supplementary Table 2 contains additional information about the pesticides, including their nonagricultural uses. The online version of this article includes an interactive map of the sites as supplementary geospatial information.

Pesticide concentration trends in these major rivers potentially reflect various combinations of large-scale changes in pesticide use (such as those due to crop changes, regulatory changes, or market forces), changes in land use (such as increased urbanization), changes in management practices (such as tillage practices, tile drainage, or conservation buffer strips), changes in climatic conditions, and other factors individually or in combinations that were prevalent in their respective regions. Generally, trends were only assessable for pesticides that were used extensively, are relatively water soluble, or are persistent enough to be frequently detected in filtered water at sampling sites, because these conditions result in sufficient detections for trend analysis.

The major contribution of this study compared to the previous Corn Belt and urban pesticide trend studies is that this study incorporates recently compiled agricultural use data for the compounds and compares and contrasts the concentration and use trends for major rivers distributed throughout the US. By identifying the directions, magnitudes, and statistical significance of trends, in context with changes in

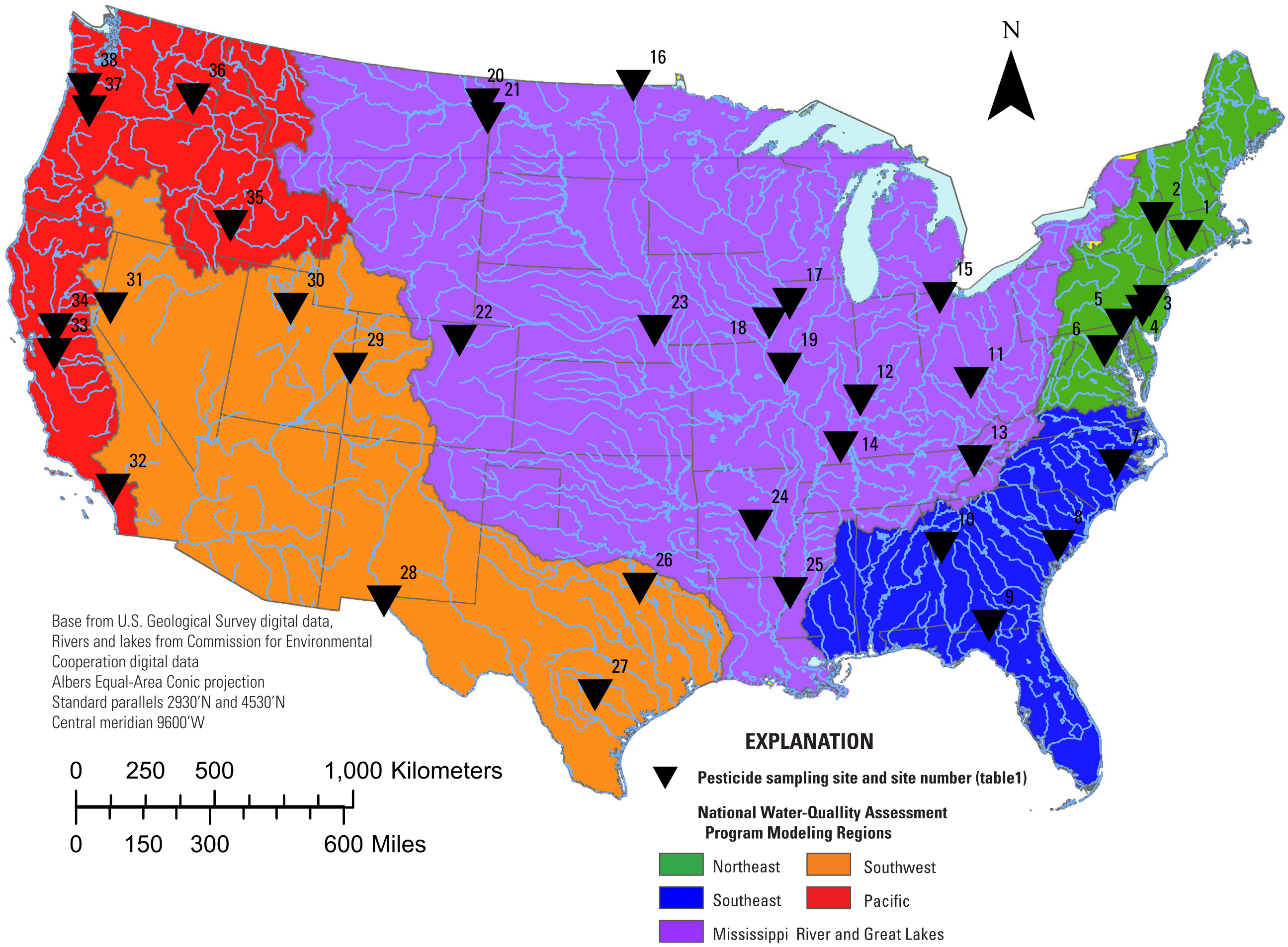

Fig. 1. Pesticide sampling sites on major rivers of the United States. Sites are described by number in Table 1.

Table 1
Sampling sites on major rivers of the United States analyzed for pesticide trends during 1992–2010, grouped by geographic regions (Fig. 1).

Site number	Site short name	USGS station number	Site name
Northeast			
1	CONNR	01184000	Connecticut River at Thompsonville, Conn.
2	MOHWK	01357500	Mohawk River at Cohoes, N.Y.
3	DELA-TR	01463500	Delaware River at Trenton, N.J.
4	SCHYL	01474500	Schuylkill River at Philadelphia Pa.
5	SUSQU	01578310	Susquehanna River at Conowingo, Md.
6	POTOM	01646580	Potomac River at Chain Bridge, at Washington, D.C.
Southeast			
7	NEUS-KN	02089500	Neuse River at Kinston, N.C.
8	EDIST	02175000	Edisto River near Givhans, S.C.
9	WTHLC	02318500	Withlacoochee River at U.S. Highway 84 near Quitman, Ga.
10	CHATT	02338000	Chattahoochee River near Whitesburg, Ga.
Mississippi River and Great Lakes			
11	OHIO-GU	03216600	Ohio River at Greenup Dam near Greenup, Ky.
12	WHITE	03374100	White River at Hazleton, Ind.
13	NOLCH	03467609	Nolichucky River near Lowland, Tenn.
14	TENNS	03609750	Tennessee River at Highway 60 near Paducah, Ky.
15	MAUM	04193500	Maumee River at Waterville, Ohio
16	REDRV	05102490	Red River of the North at Pembina, N. Dak.
17	MSSP-CL	05420500	Mississippi River at Clinton, Iowa
18	IOWA-WAP	05465500	Iowa River at Wapello, Iowa
19	ILLI-VC	05586100	Illinois River at Valley City, Ill.
20	MIZZ-CB	06185500	Missouri River near Culbertson, Mont.
21	YLOW-SN	06329500	Yellowstone River near Sidney, Mont.
22	SPLT-KR	06754000	South Platte River near Kersey, Colo.
23	PLATTE	06805500	Platte River at Louisville, Nebr.
24	ARKNS	07263620	Arkansas River at David D. Terry Lock and Dam, below Little Rock, Ark.
25	YAZOO	07288955	Yazoo River below Steele Bayou, near Long Lake, Miss.
Southwest			
26	TRNTY	08057410	Trinity River below Dallas, Tex.
27	SNANT	08181800	San Antonio River near Elmendorf, Tex.
28	RIOG-EP	08364000	Rio Grande at El Paso, Tex.
29	COLO-SL	09163500	Colorado River near Colorado-Utah State Line, Colo.
30	JORDN	10171000	Jordon River at Salt Lake City, Utah
31	TRUCK	10350500	Truckee River at Clark, Nev.
Pacific			
32	SANTA	11074000	Santa Ana River below Prado Dam, Calif.
33	SJQUN	11303500	San Joaquin River near Vernalis, Calif.
34	SACRA	11447650	Sacramento River at Freeport, Calif.
35	SNAK-KH	13154500	Snake River at King Hill, Idaho
36	PLOUS	13351000	Palouse River at Hooper, Wash.
37	WILMT	14211720	Willamette River at Portland, Oreg.
38	CLUM-QY	14246900	Columbia River at Beaver Army Terminal, near Quincy, Oreg.

use during decadal periods and with previously reported concentration trends in urban streams, this study provides a further step toward understanding the causes of long-term pesticide concentration trends in different regions of the US.

2. Methods

2.1. Concentration data

The 38 major river sites analyzed are a subset of 212 stream sites that were sampled by the U.S. Geological Survey (USGS) as part of the National Water-Quality Assessment (NAWQA) Program studies and the U.S. Geological Survey National Stream Quality Accounting Network (NASQAN). These sites were selected as part of a national set of sites that have adequate pesticide concentration data for trend analysis (Martin et al., 2011). The 38 sites represent non-nested basins with drainage areas larger than 2590 km^2 (1000 mi^2).

Water-quality sample collection strategies varied by site and varied in some years, but followed guidelines established by the NAWQA and NASQAN Programs (Crawford, 2004; Gilliom et al., 1995). Both fixed-interval and high-flow sampling procedures were used to collect samples representative of the hydrologic regimes on individual rivers. Flow-weighted, depth- and width-integrated water samples were collected using isokinetic samplers and processed following USGS methods (U.S. Geological Survey, n.d.; Shelton, 1994; Edwards and Glysson, 1999). All samples were filtered using pre-combusted glass-fiber filters with a nominal 0.7-micrometer pore diameter to remove suspended particulate matter and collected in baked amber glass bottles (Ryberg et al., 2014).

All water-quality samples were analyzed by the USGS National Water Quality Laboratory (NWQL) using a gas chromatography/mass spectrometry (GCMS) method (Zaugg et al., 1995). In this method, pesticides are isolated from filtered water samples by solid-phase extraction and analyzed by capillary-column GCMS with selected-ion monitoring (Zaugg et al., 1995; Lindley et al., 1996; Madsen et al., 2003). This method can be found in the National Environmental Methods Index (http://www.nemi.gov) as USGS-NWQL method O-1126-95.

Martin et al. (2011) reviewed and prepared the data for trend analysis. The data preparation included rounding of concentrations to a consistent level of precision; identification of reporting levels (for example, nondetections reported as less than 0.01 micrograms per liter), which varied over time; reassignment of the concentration values for routine nondetections (recensoring) to a consistent reporting level, the maximum value of the long-term method detection level (maxLT-MDL); adjusting concentrations to compensate for temporal changes in the recovery bias of the GCMS analytical method (Martin and Eberle, 2011); and the deletion of samples considered inappropriate for trend analysis (thinning samples to no more than one per week). In addition to the procedures used by Martin et al. (2011), at selected sites with sufficient low-level pesticide detections (quantified pesticide detections below the maxLT-MDL) the concentration for routine nondetections was lowered from the maxLT-MDL to the median concentration of the low-level detections (qlow50), a less conservative estimate of the detection limit (Ryberg et al., 2014).

Of the 52 pesticides and degradates included in the USGS GCMS method, 11 compounds with nationally assessable trends in concentration and use (defined as assessable trends in both concentration and use for one or more sites in at least three of the five NAWQA modeling regions, Fig. 1, regardless of trend period) are included in this trend analysis. The 11 compounds span a considerable range of registered uses and chemical properties that can affect environmental occurrence and trends, and have differing geographic patterns of agricultural and nonagricultural uses.

The years in which samples were collected varied considerably from site to site; therefore, to facilitate comparisons among trends from different sites, the entire sampling interval (1992–2010) was split into three overlapping 10-year trend periods: 1992–2001, 1997–2006, and 2001–2010. The minimum sampling criteria for a particular site to be considered adequately representative of a particular 10-year trend period were to have (1) at least 10 uncensored values after recensoring (calculating qlow50 where applicable and recensoring at that level), (2) at least 5 years of samples, (3) 6 or more samples in at least 2 of the first 5 years of the period, and (4) 6 or more samples in at least 2 of the last 5 years of the period.

2.2. Agricultural use data

County-level pesticide use for agriculture was estimated using methods developed by Thelin and Stone (2013). The use estimates for 1992 through 2009 were published in Stone (2013) and the

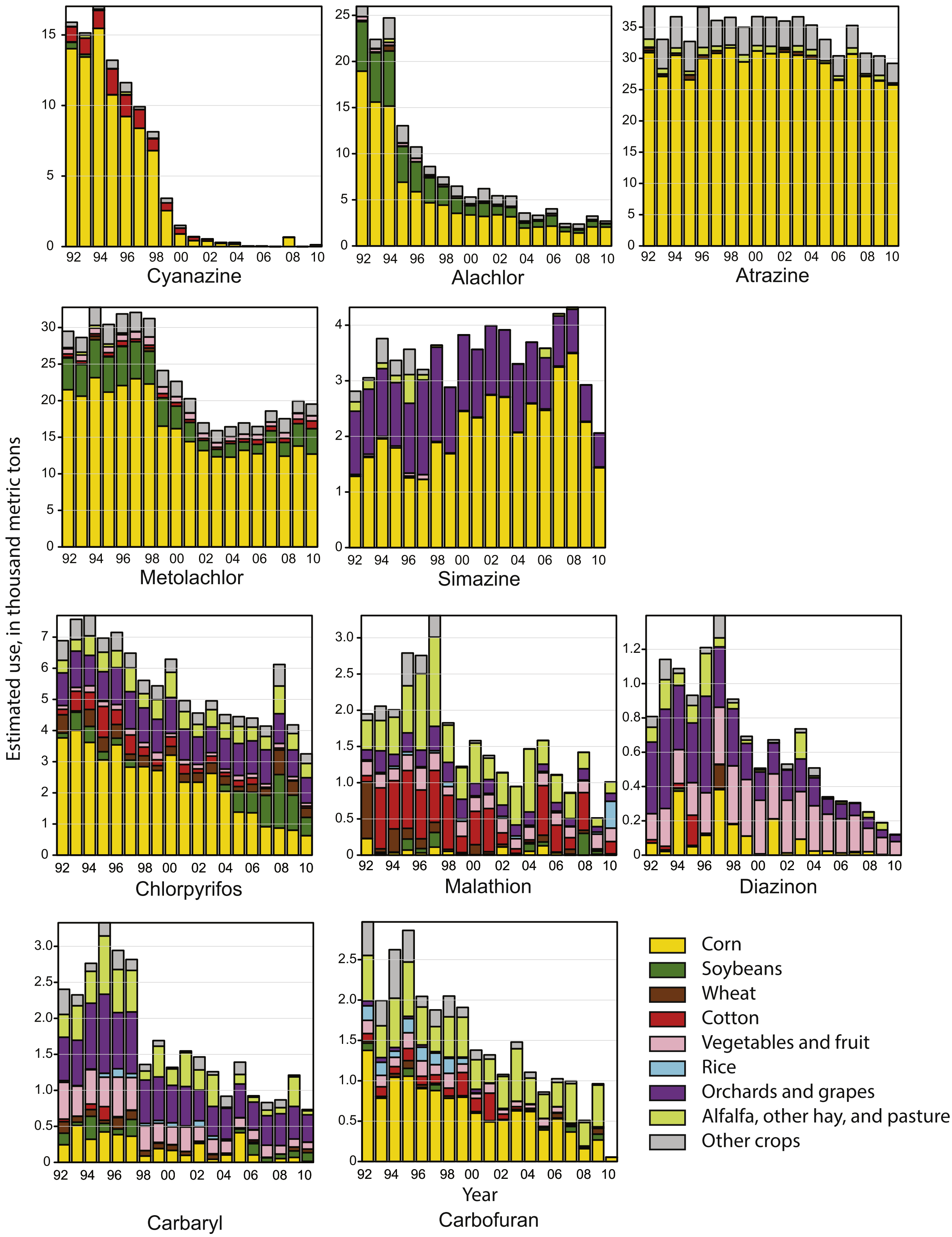

Fig. 2. National estimates of annual agricultural use during 1992–2010 for 10 pesticides for which concentration and use trends were assessed.

2010 use estimates, using the same methodology and data sources, were published in Baker and Stone (2013). The county-level use estimates include two series of annual estimates, called EPest-low and EPest-high. Both EPest-low and EPest-high "incorporated surveyed and extrapolated rates to estimate pesticide use for counties" (Thelin and Stone, 2013). The two estimates differ in how they treat missing data for pesticide-by-crop combinations. EPest-low treats missing reports as zero use. EPest-high uses a method to estimate the use based on the pesticide-by-crop use rates in surrounding areas (Thelin and Stone, 2013); therefore, EPest-high extrapolates use to a higher number of counties than EPest-low. The exceptions to this method were for sites in California, for which use estimates were obtained from annual Department of Pesticide Regulation Pesticide Use Reports (Thelin and Stone, 2013; Baker and Stone, 2013).

Annual agricultural pesticide use for each individual basin for each year was calculated by proportioning the county-level pesticide use estimates (both EPest-low and EPest-high) to the cropland in each county for all counties contained in or overlapping the basin. For counties partially within a basin, pesticide use was equal to the proportion of cropland in the county that was contained in the basin, and was obtained using a geographic information system to overlay mapped land cover with digital maps of drainage basins and county boundaries. The annual pesticide use for each basin was divided by the basin area to obtain estimated annual use intensity (kilogram per year per square kilometer). For those basins with area outside of the United States (Supplementary Table 3), the annual use intensity is the agricultural use within the United States per year divided by the basin area within the United States (N.T. Baker, U.S. Geological Survey, written communication, 2013).

2.3. Concentration trend model and analysis periods

Concentration trends were evaluated using the SEAWAVE-Q model (Vecchia et al., 2008; Sullivan et al., 2009; Ryberg and Vecchia, 2013). SEAWAVE-Q is a parametric regression model specifically designed for analyzing seasonal- and flow-related variability and trends in pesticide concentrations. This model was selected for this study based on Sullivan et al. (2009) who compared several methods for analyzing trends in pesticide concentrations for 31 sites and 11 pesticides, including several pesticides in this study. Methods compared included the seasonal Kendall test for non-flow-adjusted concentrations, a parametric regression model with seasonality and trend called SEAWAVE, and SEAWAVE-Q. The best approach in terms of maximizing the number of sites and pesticides that could be assessed and accounting for variable streamflow conditions when comparing trends for multiple sites and pesticides was determined to be the SEAWAVE-Q model. Based on those results (Sullivan et al., 2009) and the model's performance in other studies (Ryberg et al., 2010 and 2014), SEAWAVE-Q was selected as the statistical tool for analyzing trends for this study.

The model is expressed as the following for each trend in concentration for each pesticide–site–period combination:

$$\text{Log}\, C(t) = \beta_0 + \beta_1 W(t) + \beta_2 LTFA(t) + \beta_3 MTFA(t) + \beta_4 STFA(t) + \beta_5 t + \eta(t) \quad (1)$$

where Log $C(t)$ denotes the base-10 logarithm of pesticide concentration in milligrams per liter; t is decimal time, in years, with respect to an arbitrary time origin; $\beta_0, \beta_1, \ldots, \beta_5$, are regression coefficients; W is a seasonal wave representing intra-annual patterns in concentration and is a dimensionless, periodic (with a period of 1 year) solution to a differential equation (defined in Vecchia et al., 2008, and visualizations provided in Ryberg and Vecchia, 2013); LTFA, MTFA, and STFA are dimensionless long-term (greater than 365 days), mid-term (30- to 365-day), and short-term (daily to 30-day) streamflow anomalies computed from daily streamflow (anomalies defined in Vecchia, 2003; and calculated using Ryberg and Vecchia, 2012); and $\eta(t)$ is the model error. The concentration trends are expressed as a percent change per year, $100(10^{\beta 5} - 1)$, where β_5 is the time trend coefficient. Statistical significance at the 0.10 significance level was determined using the t-test of significance of the model coefficients (Neter et al., 1996).

2.4. Use trend model

The statistical analysis followed the method of Vecchia et al. (2009), where trends in agricultural use for each pesticide–site–period combination were obtained by linear regression:

$$\log UI(t) = \beta_0 + \beta_1 t + \varepsilon(t) \quad (2)$$

where log $UI(t)$ is the base-10 logarithm of pesticide use intensity (kilogram per year per square kilometer) for a particular pesticide–site–period combination for the year t, β_0 and β_1 are regression coefficients, and $\varepsilon(t)$ is the model error for the year t.

Both time series of use estimates (EPest-low and EPest-high) contain some years in which use was reported as zero. This seems unlikely in some cases given the crops grown in the basins and the estimates in the years immediately preceding and following the zero estimates. In addition, the trend model used is based on the logarithm of use intensity and, therefore, zero values cannot be used. Treating the zeroes as missing values was considered; however, with annual use-intensity estimates from 1992 to 2010 only, the number of observations is already small and reducing the number resulted in many series too short for reliable trend analysis. For these reasons, only those pesticide–site–period combinations with no zero values for either EPest-low or EPest-high were used for trend analysis. Because there were two estimates of pesticide usage, Eq. (2) was implemented as interval-censored regression (Therneau, 2013) to incorporate both of the estimates. When the EPest-low and EPest-high estimates differed, the value used in the regression model was an interval, censored between the two estimates. When the two estimates were the same, a single, noncensored value was used in the regression model. A parametric survival regression model was fit using maximum likelihood methods for censored data (Therneau, 2013). In a small number of cases, despite sufficient data, the survival regression method could not converge on a solution for the parameter estimates. The use trends are expressed as a percent change per year, $100(10^{\beta 1} - 1)$, where β_1 is the trend coefficient. Statistical significance at the 0.10 significance level was determined using the t-test of significance of the model coefficients.

2.5. Limitations

When comparing the pesticide concentration trends and the use trends, several factors should be considered when interpreting them:

- The use trends are for agricultural use only, whereas the concentration trends integrate all pesticide sources and some pesticides have substantial nonagricultural uses.
- Annual agricultural use estimates for a pesticide have unspecified uncertainty. In general, estimates for low-use areas and for low-use crops are expected to be the most uncertain, whereas estimates for high-use areas and crops are expected to be most reliable.
- The use trends are based on only 10 annual values, so there is a low power for trend detection.
- Trends for particular cases often could not be calculated for both concentration and agricultural use when one or more of the following was true: concentration samples were not representative of a particular period, concentration data were too highly censored for trend analysis, there were less than 10 years of nonzero use estimates for one or both EPest-low and EPest-high, or the interval-censored regression model was unable to converge on a solution for the use trends. These particular cases limit opportunities for site-by-site comparisons of concentration and use trends.
- Pesticides that are environmentally persistent may have concentration trends that lag a decrease in use intensity.
- There may have been changes in agricultural management practices (such as tile drainage, tillage practices, or conservation buffer strips) that changed the relative amount of agricultural pesticide reaching the stream, independent of use trends.

3. Results and discussion

Results are organized in two groups of pesticide compounds: (1) five herbicides (and one degradation product) having little or no nonagricultural use, in terms of mass applied, with the exception of simazine, and (2) five insecticides, most of which have lower use than the herbicides, substantial nonagricultural use, and for which use trends are thus less completely and reliably quantified. Results for pesticide–site–period combinations (cases) with adequate data for analysis are summarized in two types of graphs—one that shows concentration trends with confidence bounds, and one that shows the relation between concentration and agricultural-use trends. Results, where possible, also were compared to potential changes in nonagricultural uses, as indicated by concentration trends in the same compounds in a study of urban streams (Ryberg et al., 2010).

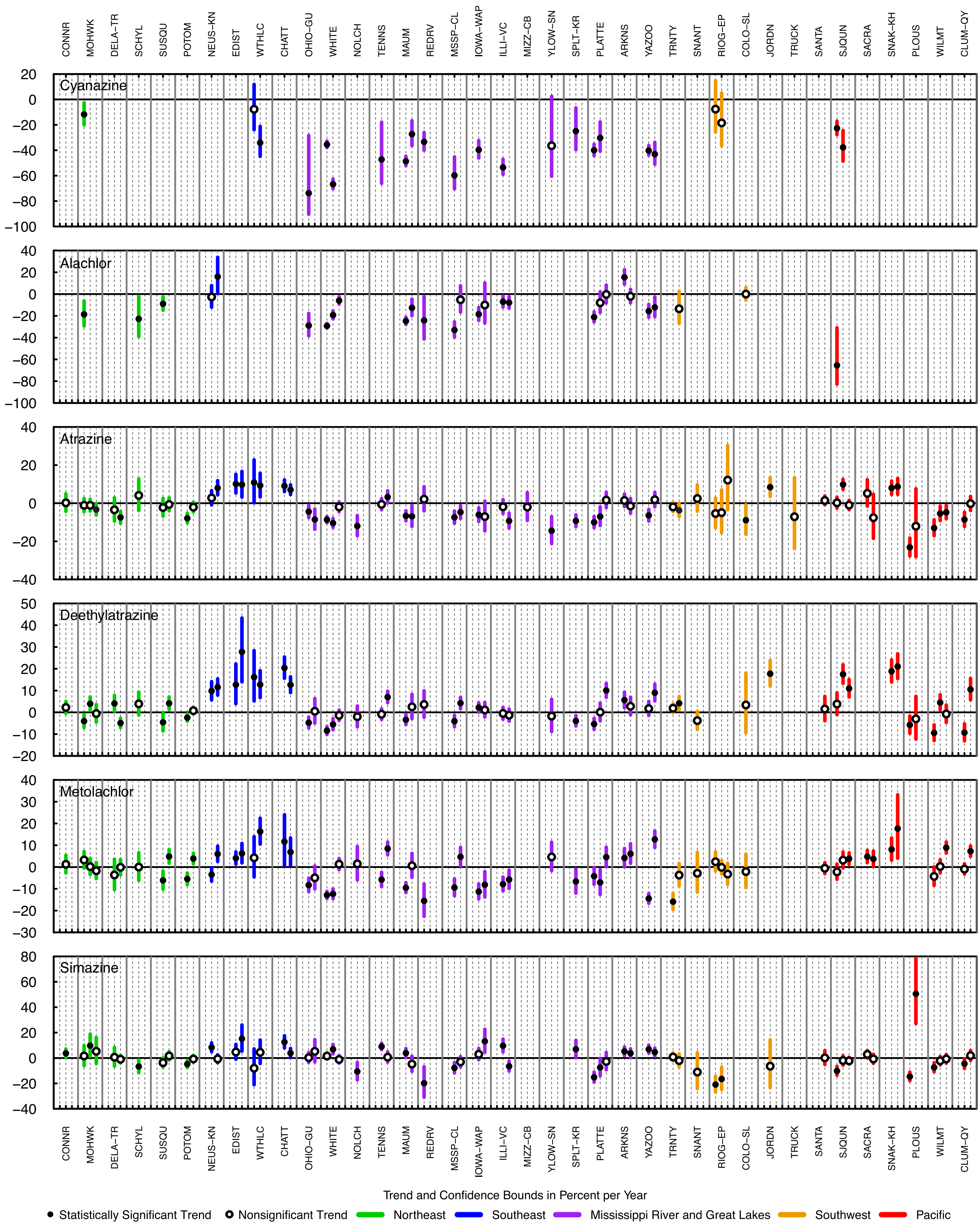

Fig. 3. Herbicide concentration trends for 38 rivers during three overlapping trend analysis periods, 1992–2001, 1997–2006, and 2001–2010. Site short names are defined in Table 1. Trends are indicated by black dots with 90-percent confidence bounds extending above and below the trend. The three analysis periods are shown as three dashed lines, with the earliest time period on the left, for each site with trends and confidence bounds on top of the dashed lines. In many cases trends were not assessable in all three periods.

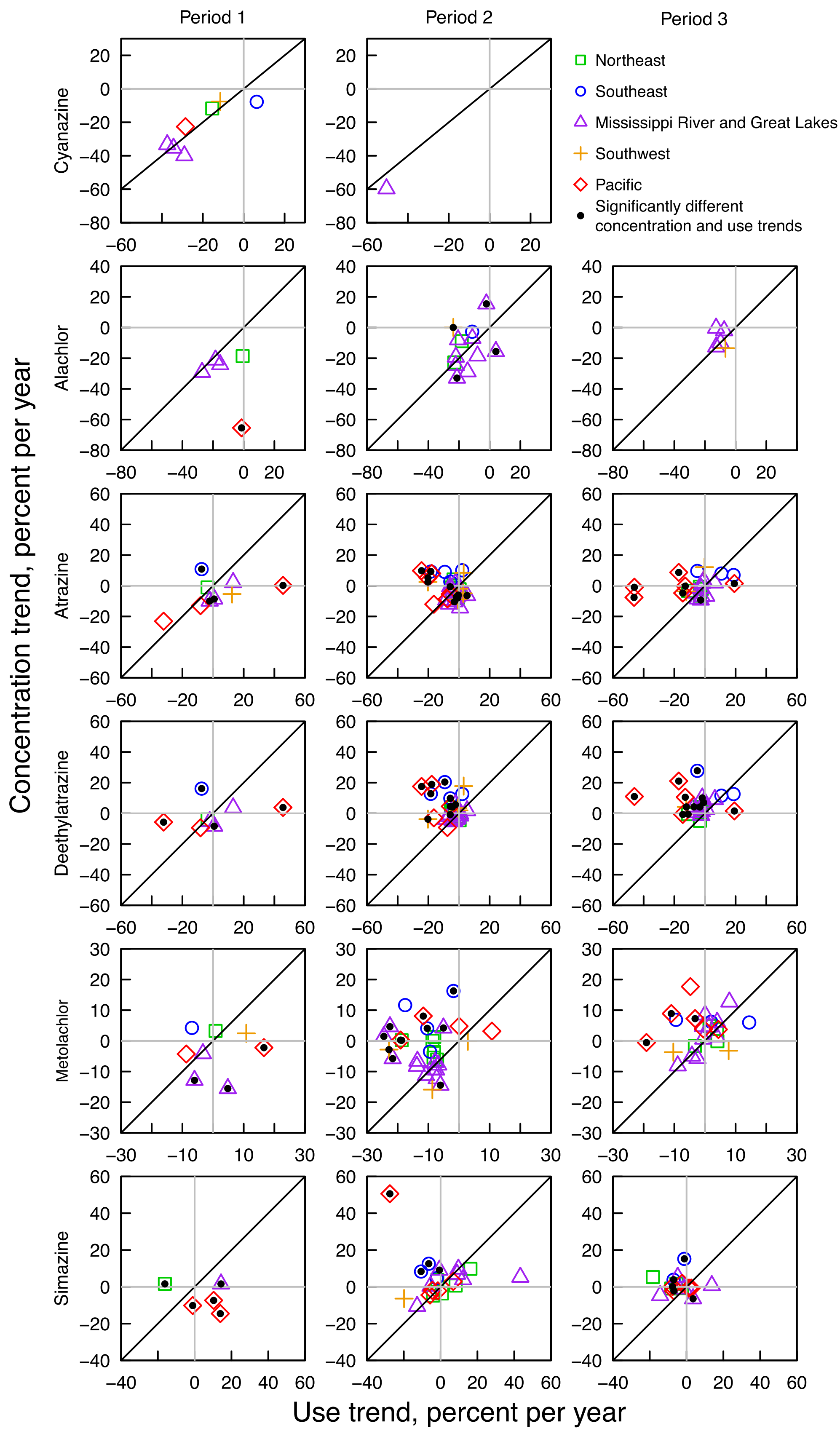

Fig. 4. Herbicide concentration trends (y-axis) and agricultural use trends (x-axis) at sites with paired trends. Deethylatrazine concentration trends are paired with atrazine use trends. There are no paired trends for cyanazine in the third period. Concentration and use trends were deemed significantly different when 90-percent confidence bounds did not overlap. Period 1, 1992–2001; Period 2, 1997–2006; Period 3, 2001–2010.

3.1. Herbicides

All five herbicides—cyanazine, alachlor, atrazine, metolachlor, and simazine—were primarily used on corn, but each has a distinctive history of national use (Fig. 2). Results of trend analysis are presented and discussed for each herbicide below. Concentration trend results are shown in Fig. 3. Paired trends for concentration and use are shown in Fig. 4. The figures summarize the results and show geographic patterns, whereas concentration and use trends, in percent per year, and associated *p*-values, are provided in Supplementary Table 4 and can be used to sort and summarize the trends in additional ways.

3.1.1. Cyanazine

National use of cyanazine averaged over 15 thousand metric tons (TMT) annually during 1992–1994, then declined steadily through 1998 (Fig. 2). Cyanazine registration was then canceled in 1999 and sales were rapidly phased out through 2002 (U.S. Environmental Protection Agency, 2000), although some agricultural use was still reported in the following years (Stone, 2013).

All but two concentration trends were for 1992–2001 and 1997–2006, periods that still included substantial cyanazine use, and most were rivers in the Mississippi River and Great Lakes region with substantial corn production. Of seven sites with concentration trends for 1992–2001, five had significant downtrends and two had nonsignificant trends. For 1997–2006, 12 sites had significant downtrends and two had nonsignificant trends.

The consistency of concentration trends with national use trends was corroborated by site-specific comparisons of concentration and use trends for 1992–2001 (use trends generally could not be computed for the second and third analysis periods because of zero reported use at most sites after about 2000). Fig. 4 shows high correspondence between concentration and use trends for seven sites, with none of the sites having significant differences between concentration and use trends.

3.1.2. Alachlor

Annual use of alachlor averaged over 20 TMT during 1992–1994 (Fig. 2). Then, similar to cyanazine, use declined rapidly to about 5 TMT by about 2000. During the following decade, ending in 2010, alachlor use gradually declined an additional 50%, from 5 to 2.5 TMT. In contrast to cyanazine, alachlor use continued through the end of the study period with a more gradual, but steady, decline than seen with cyanazine. According to Sullivan et al. (2009), alachlor use declined because of two main factors: the introduction of acetochlor in 1994 (which widely replaced alachlor for corn) and the introduction and steady increase in use of glyphosate-resistant soybeans and corn (reducing the need for alachlor).

Consistent with the history of national use, downward trends in concentrations of alachlor are evident across the nation during all analysis periods, particularly in the Mississippi River and Great Lakes region, with 18 significant downtrends, 8 nonsignificant trends, and only 2 significant uptrends (Fig. 3). The magnitude of downtrends generally decreased from the first to the third analysis periods.

Site-specific comparisons (Fig. 4) show that most concentration and use trends were not significantly different from each other. Across all analysis periods, 5 of 23 combinations of concentration and use trends were significantly different, with three differences due to concentration trends less than use trends (either more negative or less positive) and two differences due to concentration trends greater than use trends. There are no clear differences between regions in the trend results except that many more sites could be analyzed for the Mississippi River and Great Lakes region, where alachlor was most heavily used. Whereas cyanazine had few sites with adequate data to assess after the first analysis period, the continued use of alachlor enabled assessments of both concentrations and use at some sites and results show generally decreasing downward trends from 1997–2006 to 2001–2010, which corresponds to the slowing decline in use.

3.1.3. Atrazine and deethylatrazine

National agricultural atrazine use was relatively stable during 1992–2004, averaging about 35 TMT, with most used on corn (Fig. 2). Use then declined approximately 15% during 2004–2010, a far smaller decline than for cyanazine or alachlor. Deethylatrazine (DEA) is one of the primary degradation products of atrazine and is evaluated in relation to the use of atrazine. In the 1990s, the U.S. Environmental Protection Agency's Office of Water began to regulate atrazine under the Safe Drinking Water Act (U.S. Environmental Protection Agency, 2009) and risk reduction measures, including decreased application rates for some crops and non-crop uses and well-head protection measures, were instituted to address concerns about surface-water contamination (U.S. Environmental Protection Agency, 2006a).

Considering all sites and assessment periods, atrazine concentration trends were consistent with the history of relatively steady to slightly declining national use, with overall prevalence of nonsignificant trends and significant downtrends. During 1992–2001, for which there were only nine assessable sites, four sites had nonsignificant trends, four sites had significant downtrends, and one site had a significant uptrend. For the second assessment period, 1997–2006, there were 36 assessable sites—16 that had no significant trend, 14 that had significant downtrends (10 in the Mississippi River and Great Lakes region; Fig. 3), and 6 that had significant uptrends (3 in the Southeast). The more frequent occurrence of downtrends in the Mississippi River and Great Lakes region is consistent with the gradual national decline in atrazine use on corn during that period and the uptrends at Southeast sites may reflect possible increasing use of atrazine on turf grass, which was not included in agricultural use estimates. For the third assessment period, 2001–2010, there was a smaller proportion of downtrends even though national use declined.

The magnitudes of both uptrends and downtrends in atrazine concentrations were relatively small, with most in the range of 10% per year or less, but there are some distinct regional patterns. For sites in the Mississippi River and Great Lakes region, where atrazine was heavily used, all trends were nonsignificant or downward, with all but one trend less than 10% per year. Rivers in the Northeast followed a similar pattern as the Mississippi River and Great Lakes region, but with a smaller proportion of downtrends and more nonsignificant trends. The most striking regional difference from the Mississippi River and Great Lakes region pattern of trends is the proportion of significant uptrends for Southeast sites. Results for the Southwest and Pacific regions, where atrazine use was generally least, were much more variable site to site and no consistent patterns were evident within these regions.

Trends in DEA concentrations were notably different from atrazine trends during the second and third analysis periods, when most sites could be evaluated, although general regional patterns were similar. During 1997–2006, and particularly 2001–2010, there were more uptrends than downtrends in DEA concentrations compared to atrazine. During 2001–2010, 12 sites had significant uptrends in DEA and only 1 had a significant downtrend, whereas atrazine had 5 significant uptrends and 8 significant downtrends and more nonsignificant trends.

Most concentration trends were not significantly different from use trends and most cases in all three periods plot within 10% of the 1:1 line (representing equal concentration and use trends, Fig. 4). Most cases with significant differences between use and concentration trends are sites in the Pacific or Southeast regions, although there are also a few such cases in other regions that have small differences in trend magnitudes. With only two exceptions, all cases with significantly different concentration and use trends in the Pacific and Southeast rivers are cases with use downtrends paired with concentration trends that are either upward or less downward. This pattern is consistent with the possibilities of: (1) failure to account for certain uses that were increasing, or (2) a lagged source, such as groundwater, which contributed DEA from past uses. Increased use of atrazine on nonagricultural turf grasses is a possible explanation for rivers in the southeast, where atrazine is a common herbicidal treatment of certain lawn grasses (U.S. Environmental Protection Agency, 2006a). In addition, most significant differences between concentration and use trends were for cases in which DEA had substantially greater uptrends in concentration than atrazine.

The occurrence of uptrends in DEA concentrations for sites and periods with significant downtrends in both the use and concentrations of atrazine could be caused by some factor, such as a management practice, that has increased over time the proportion of applied atrazine that runs off to streams as DEA, or by a transport pathway for DEA, such as groundwater, that has multi-year lags between use and arrival at a stream. Gilliom et al. (2006) reported that DEA-to-atrazine ratios were generally higher in groundwater than streams, which likely reflects soil microorganism degradation of atrazine because of the longer periods of soil contact time for the atrazine compounds detected in the groundwater system, relative to streams. Thus, increased concentrations of DEA in groundwater contributed to streams—resulting from high rates of past atrazine use where the groundwater originated—could explain the uptrends in some streams. Another possibility is that a management practice, such as no-till agriculture, resulted in longer residence time of atrazine in soil and a greater amount of transformation to DEA before runoff to a stream.

3.1.4. Metolachlor

Metolachlor had relatively steady national use during 1992–1998, a substantial reduction in use during 1998–2003, and then increasing use from 2003–2010 (Fig. 2). A reformulation of metolachlor, S-metolachlor, was introduced in 1996, which resulted in effective weed control with less metolachlor (Sullivan et al., 2009; the amount used for use trend analyses is the sum of metolachlor and S-metolachlor because they are both analyzed as metolachlor in chemical analyses of water samples). As S-metolachlor was phased into use, it had mostly replaced metolachlor by 2002, with total use of both forms at a combined total of about one-half the amounts used in 1996 and 1997. Since about 2004, the use of metolachlor has been gradually increasing. This is likely because of increases in corn acreage in the US. Total acres planted to corn in 2001 were 75,702,000, whereas in 2010 the total acreage was 88,193,000 (U.S. Department of Agriculture National Agricultural Statistics Service, 2014).

Metolachlor had mixed patterns of concentration downtrends and uptrends depending on region and period (Fig. 3). Regionally and across analysis periods, sites in the Northeast and Southwest mostly had insignificant or small trends, sites in the Southeast and Pacific had more uptrends than downtrends, and sites in the Mississippi River and Great Lakes region had more downtrends than uptrends. During 1992–2001, there were three significant downtrends in concentration—all sites in the Mississippi River and Great Lakes region. During 1997–2006, there were 32 assessable sites, with 14 of 20 significant trends being downward. Consistent with the trend in national use, the pattern reversed during 2001–2010, with 15 of 25 assessable sites having significant uptrends compared to only 2 with significant downtrends.

Comparisons of use and concentration trends for the subset of sites for which both could be evaluated (Fig. 4) show how use and concentration patterns changed across time. During 1992–2001, three of eight sites had significantly different use and concentration trends, with all three having greater declines in concentration compared to use. As use trends shifted to more broadly downward during 1997–2006, most sites had similar use and concentration trends (not significantly different and mostly downward). Ten of the 11 sites with significant differences between use and concentration trends, however, had greater declines in use compared to concentrations (several of which increased). During the last analysis period, 2001–2010, the overall frequency of uptrends increased in correspondence to increasing use, but the contrary pattern observed for 1997–2006 continued, with three sites in the Pacific region having significantly greater concentration trends (confidence interval contained 0 or was completely above 0) than use trends (confidence intervals were completely below 0), possibly because of unaccounted uses.

3.1.5. Simazine

National agricultural use of simazine erratically increased during 1992–2008, with use on orchards and grapes generally declining and use on corn increasing, and then dropped more than 50% during 2008–2010 (Fig. 2). Simazine also has many nonagricultural uses totaling more than 0.5 TMT per year, including weed control in turfgrass, right-of-ways, industrial sites, commercial and residential lawns, and golf courses (U.S. Environmental Protection Agency, 2006c), but trends in those uses are not known. Ryberg et al. (2010) detected many significant uptrends in simazine concentration for urban streams during similar periods (1996–2004 and 2000–2008), suggesting that some nonagricultural uses have been increasing.

For 1992–2001, six of nine assessable sites had significant downtrends in simazine concentrations, with the rest being nonsignificant. All six sites with downtrends are in the Pacific, Southwest, or western part of the Mississippi River and Great Lakes regions. A possible contributor to the concentration decline is a decline of agricultural use on “alfalfa, other hay and pasture,” and on “other crops” during this period. These reductions in use may have been more prevalent in the western US. For 1997–2006, 31 sites had adequate data for analysis of concentration trends—12 with uptrends, 7 with downtrends, and 12 nonsignificant. Most of the uptrends are in the Mississippi River and Great Lakes region where corn is the major crop with simazine use. These results are consistent with Sullivan et al. (2009), who found that simazine concentrations in the Corn Belt generally increased during a similar period (1996–2006). For the third period, 2001–2010, results are generally similar to 1997–2006, but with fewer statistically significant trends.

Comparisons of simazine use and concentration trends for the subset of sites for which both could be evaluated (Fig. 4) show how concentration and use patterns changed across time. During 1992–2001, all five sites had significantly different use and concentration trends, with four of the five having greater declines in concentration compared to use. These sites may have had use declines that were greater than estimated from available agricultural use data, or declines in nonagricultural uses. During 1997–2006, only 4 of 21 sites had significant differences between concentration and use trends, with all 4 having upward concentration trends and downward or nonsignificant use trends. The same general pattern was found for 2001–2010, with 5 of 16 sites having significant differences, and all but one having concentration trends more upward or less downward than use trends. The overall pattern for the second and third evaluation periods, when most assessable cases were available, is consistent with concentration trends being generally small and driven by agricultural use, but with nonagricultural uses tending to increase and cause some sites with concentration increases (or reduced declines) greater than expected from changes in agricultural use.

3.2. Insecticides

Trend results for concentrations and agricultural-use of the insecticides chlorpyrifos, malathion, diazinon, carbaryl, and carbofuran are shown in Fig. 5. Paired trends for concentration and use are shown in Fig. 6. The figures summarize the results and show geographic patterns. Concentration and use trends, in percent per year, and associated *p*-values, are provided in Supplementary Table 5 and can be used to sort and summarize the trends in additional ways.

3.2.1. Chlorpyrifos

National agricultural use of chlorpyrifos steadily declined from about 7 to 3 TMT during 1992–2010, with the exception of 2008

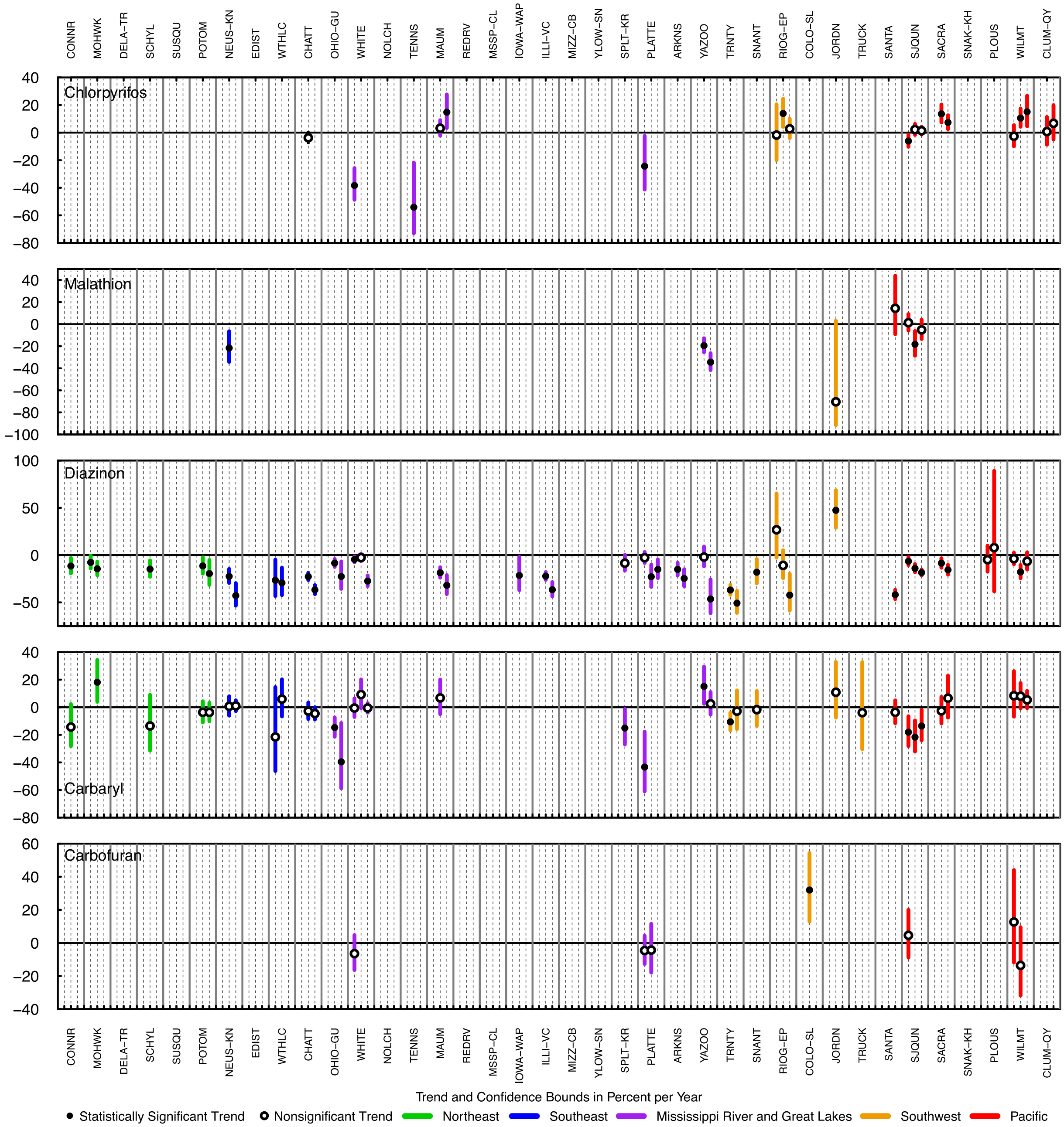

Fig. 5. Insecticide concentration trends for 38 rivers during three overlapping trend analysis periods, 1992–2001, 1997–2006, and 2001–2010. Site short names are defined in Table 1. Trends are indicated by black dots with 90-percent confidence bounds extending above and below the trend. The three analysis periods are shown as three dashed lines, with the earliest time period on the left, for each site with trends and confidence bounds on top of the dashed lines. In many cases trends were not assessable in all three periods.

(Fig. 2). Declining use on corn accounted for most of the overall use decline, whereas use on soybeans increased during 2004–2010, and use on a variety of other crops remained relatively consistent. Nonagricultural use of chlorpyrifos has historically been in the range of 2.3–4.1 TMT per year (1999 estimate from Donaldson et al., 2002), but has declined because of 1997–2005 phase outs of residential and termite uses (in order to reduce indoor and residential exposures) and reductions in applications rates for outdoor areas, including road medians, industrial sites, and golf-course turf (U.S. Environmental Protection Agency, 2002). Ryberg et al. (2010) found mainly downtrends in chlorpyrifos concentrations in urban streams during 1992–2008, consistent with nonagricultural uses decreasing.

Chlorpyrifos has few assessable sites for concentration trends in all three periods because of high levels of censoring resulting from nondetections in surface-water samples; it is a hydrophobic compound with a relatively short half-life (half-life for non-photolytic transformation in soil 30.5 days and in water 29 days; Supplementary Table 1; Gilliom et al., 2006). Five sites were assessable for concentration trends during 1992–2001—three had significant downtrends and two nonsignificant trends (Fig. 5). During 1997–2006 and 2001–2010, there were six uptrends, seven nonsignificant trends, and only one downtrend. The finding of more uptrends than downtrends since 1997 is unexpected given the general decline in agricultural use and phaseouts and application rate reductions in nonagricultural uses. In contrast, Ryberg et al. (2010) found significant downtrends in chlorpyrifos concentration for 9 out of 10 urban sites that could be analyzed for a period similar to the second trend period (1996–2004), which is evidence that the phase out of residential uses is associated with downward concentration trends in urban streams. The unexpected

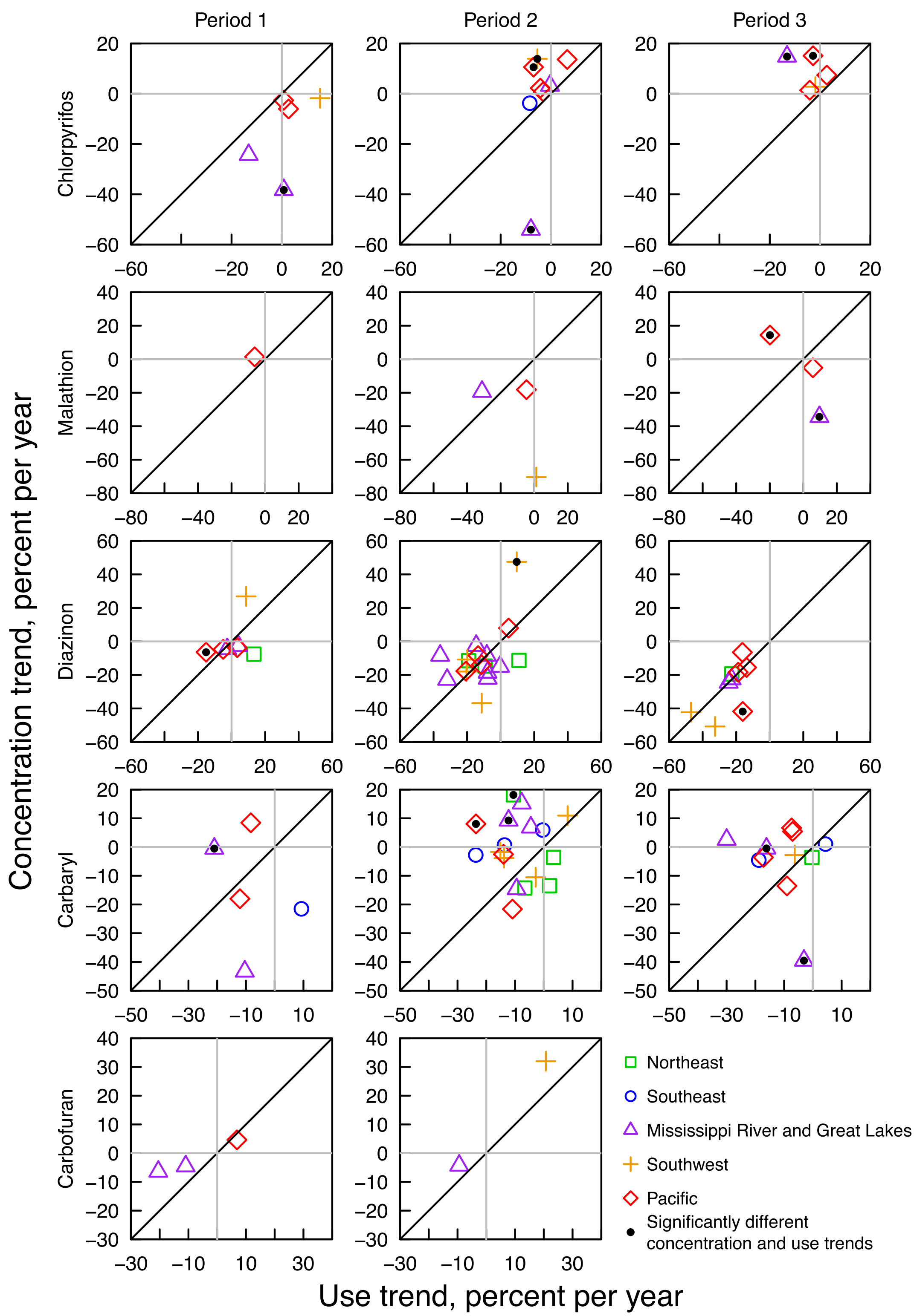

Fig. 6. Insecticide concentration trends (y-axis) and agricultural use trends (x-axis) at sites with paired trends. There are no paired trends for carbofuran in the third period. Concentration and use trends were deemed significantly different when 90-percent confidence bounds did not overlap. Period 1, 1992–2001; Period 2, 1997–2006; Period 3, 2001–2010.

prevalence of concentration uptrends since 1997 may be due to an increase in agricultural use or other rural use not adequately accounted for in use estimates. The uptrends are unlikely to be delayed transport by groundwater because of the hydrophobic character of chlorpyrifos. Chlorpyrifos is classified as strong for sorption to soil (Supplementary Table 1; Ryberg et al., 2014). Although runoff events could transport soil particles with adsorbed chlorpyrifos to streams, all of the samples analyzed for this study were filtered and represent estimates of dissolved concentration.

Site-by-site comparisons for chlorpyrifos show that most cases—12 of 18—had insignificantly different concentration and use trends (Fig. 6), despite the incongruities noted above. Across all three analysis periods, two cases with significant differences had large concentration downtrends with little or no downtrend in agricultural use. Four cases with significant differences—all in the second two periods—had concentration uptrends despite relatively small downtrends in use.

3.2.2. Malathion

Malathion has been used on a wide variety of crops, with the largest amounts over time applied on cotton and “alfalfa, other hay, and pasture” (Fig. 2). Historically, annual agricultural use increased during 1992–1997 from 2 to over 3 TMT, dropped quickly back below 2 in 1998, and then erratically declined to about 1 TMT by 2010. Nonagricultural uses were estimated in the range of 1.4–3.2 TMT per year during approximately 2001–2007 (Grube et al., 2011), and thus, relative to agricultural use are a significant potential influence on concentration trends in many rivers. Ryberg et al. (2010) found that all assessable trends in urban streams (many streams were not assessable because of inadequate detections) were downward during 1992–2008, with about a third of the downward trends statistically significant.

Across all three analysis periods, all four significant concentration trends for malathion in the rivers evaluated are downtrends, compared to four nonsignificant trends (Fig. 5). Malathion is short-lived in soil and water (half-life for non-photolytic transformation in soil less than 1 day and in water 6.3 days; Supplementary Table 1; Gilliom et al., 2006) and thus only low concentrations and frequent nondetections are common in major rivers. For the seven site-period combinations for which concentration and agricultural-use trends could be compared, two were significantly different, with one in each direction (Fig. 6).

3.2.3. Diazinon

Diazinon has historically been used for pest control on a wide variety of crops, with the greatest amounts applied to “vegetables and fruit” and “orchards and grapes” (Fig. 2). Total annual agricultural use increased erratically from 0.8 to 1.4 TMT during 1992–1997, but then declined about 90% from 1997–2010 to a low of about 0.1 TMT. Overall, there was a decline in agricultural use in all three trend analysis periods. All indoor and outdoor residential uses of diazinon have been canceled and sales were phased out, ending December 31, 2004 (U.S. Environmental Protection Agency, 2006b, 2008b). Ryberg et al. (2010) found widespread downtrends of diazinon concentrations in urban streams from 1992–2008.

Diazinon concentration trends follow the downtrends in both agricultural and nonagricultural use. During 1992–2001, there were 4 significant downtrends and 4 nonsignificant trends; 1997–2006 had 18 significant downtrends, 1 significant uptrend, and 5 nonsignificant trends; and 2001–2010 had 15 significant downtrends and only 1 nonsignificant trend. Most of the downtrends during the last assessment period were in the range of minus 20 to 50% annually (Fig. 5).

Site-by-site comparisons for diazinon show that 31 of 34 cases across all three analysis periods had insignificantly different concentration and use trends. Of the three cases with significant differences, two had concentration trends that were more upward or less downward than the corresponding use trend and one case was the opposite (Fig. 6).

3.2.4. Carbaryl

Carbaryl has historically been used for pest control on a wide variety of crops, with the greatest amounts applied to “orchards and grapes”, “vegetables and fruit”, and “alfalfa, other hay, and pasture” (Fig. 2). Total annual agricultural use increased from about 2.4 to 3.5 TMT during 1992–1995, but then declined about 80% from 1995–2010 to a low of about 0.75 TMT. Overall, there was a decline in agricultural use in all three trend analysis periods. Nonagricultural uses of carbaryl have been estimated at 0.91 TMT (1998 data; U.S. Environmental Protection Agency, 2004). In March 2005, the U.S. Environmental Protection Agency canceled liquid broadcast of carbaryl on residential turf and issued requests for additional studies and data. Since the requests, many technical registrants voluntarily canceled their products (U.S. Environmental Protection Agency, 2007a and 2008a). Ryberg et al. (2010) found that carbaryl concentration trends in urban streams were mostly nonsignificant: 15 of 21 sites during 1996–2004 and 15 of 21 sites during 2000–2008.

Five sites were assessable for concentration trends during 1992–2001—two had significant downtrends and three were nonsignificant (Fig. 5). During 1997–2006 and 2001–2010, combined, there were 22 nonsignificant trends, 8 downtrends, and 2 uptrends. Over the 3 trend periods, 6 of 34 concentration-use comparisons had significant differences and all but one had upward or neutral concentration trends even though use was significantly downward in all cases (Fig. 6). This pattern suggests increases in uses within the basins of these 5 sites that were not accounted for in the agricultural use estimates.

3.2.5. Carbofuran

Carbofuran has historically been used for pest control on a variety of crops, with the greatest amounts applied to corn and “alfalfa, other hay, and pasture” (Fig. 2). Total annual agricultural use decreased from about 2.5 TMT during 1992–1995 to less than 0.5 TMT by 2010. Overall, there were erratic, but distinct, declines in agricultural use across all three trend analysis periods. Carbofuran is classified as a restricted use pesticide and the technical registrant made a number of label changes in the late 1990s to reduce drinking water and ecological risks. Risk reduction measures included reducing application rates and the reducing the number of applications for some crops and for some soils (U.S. Environmental Protection Agency, 2007b).

Concentrations of carbofuran are too highly censored for trend analysis for most sites and periods. Only seven site-period cases could be evaluated for concentration trends and all but one were nonsignificant (Fig. 5). Site-based comparisons of concentration and use trends were possible for five cases and none were significantly different (Fig. 6). The only significant trend in concentration was upward and occurred at COLO-SL, which also had a comparable uptrend in use (Fig. 6).

3.3. Relations between concentration and use trends

The analysis of relations between concentration and use trends is based on results for the site-period combinations for which both concentration and agricultural use trends could be assessed for a particular pesticide at the same site. Across all pesticides, periods, and sites, there were 385 direct comparisons of concentration and use trends (including comparison of DEA trends to atrazine use trends), with the vast majority—72%—indicating no significant differences (that is the 90-percent confidence bounds for the trends in percent per year overlapped). This finding is consistent with a previous study of herbicide trends in Corn Belt streams and rivers, which found that use trends explained most concentration trends and concluded that reductions in concentrations due to improved management practices (those unrelated to use reduction) will be difficult to discern (Sullivan et al., 2009). More precise estimates of both agricultural and nonagricultural uses and basin-wide data on specific management practices will likely be needed to assess the large-scale effects of management practices on pesticide concentrations in rivers.

Although the minority overall, comparisons between concentration and use trends for cases with significant differences provide some insight regarding factors that may influence these differences. For the second two analysis periods, 1997–2006 and 2001–2010—when most comparisons were possible, the majority of significant differences between concentration and use trends indicate that concentration trends are either more upward or less downward than corresponding use trends. Of 85 paired comparisons with significant differences, 67 had concentration trends that were greater (more upward or less downward) than the corresponding use trends. Of these 67 cases, all but 2 had downtrends in use and all but 15 had uptrends in concentrations. This pattern is the opposite of what one would expect, for example, if some broad improvement in agricultural management practices had reduced transport of pesticides to streams. Possible explanations for concentrations declining less than agricultural use, or increasing despite declining use, include:

1. Upward trends in nonagricultural uses that were not captured by the use surveys.
2. Inadvertent false trends (or nontrends) in agricultural use estimates due to characteristics of the proprietary use surveys. For example, agricultural use surveys may not have adequately characterized use trends on non-major crops, which could have had increases in use.
3. An increasing management practice, such as tile drainage, which could accelerate transport to surface waters and divert transport from much longer and slower flow paths through the groundwater system.
4. Slow transport of compounds via groundwater, such that increasing contributions of river inflow from groundwater affected by past higher use results in increased river concentrations during base flows. Atrazine degrading to DEA in the presence of soil microorganisms and later contribution of that DEA to streams via groundwater is an example.

All of these are avenues for future investigation or refinement of methodology.

The pattern of greater concentration trends than use trends, for those cases when the two are significantly different, is most prevalent for atrazine, DEA, metolachlor, and simazine. Most of the cases are in the Pacific and Southeast regions. In these two regions, as compared to the Mississippi River and Great Lakes region, there is a greater potential that uses not accounted for in the agricultural use surveys, such as in silviculture, would have a substantial proportional influence on use trends and that increases in such uses could account for the concentration trends observed.

The pesticide compound DEA, a degradate of atrazine, had the most frequent occurrences during both 1997–2006 and 2001–2010 of concentration trends in the opposite direction of use trends (atrazine use), and in some cases atrazine concentration trends. The occurrence of uptrends in DEA concentration for sites and periods with significant downtrends in both atrazine use and concentration may have been related to some factor, such as a management practice, that has increased the proportion of applied atrazine that runs off to streams as DEA, or by a transport pathway for DEA, such as groundwater, that has multiyear lags between use and arrival at a stream.

4. Conclusions

The unique contribution of this study is that it incorporates recently compiled agricultural use data for pesticide compounds with adequate water monitoring data and compares and contrasts the concentration and use trends for major rivers distributed throughout the US. By evaluating the directions, magnitudes, and statistical significance of concentration trends, in context with changes in use during decadal periods, as well as with previously reported concentration trends in urban streams, this study provides a further step toward understanding the causes of long-term pesticide concentration trends in different regions of the US.

Pesticides strongly dominated by agricultural use—cyanazine, alachlor, atrazine, metolachlor, and carbofuran—had widespread agreement between concentration trends in major rivers and use trends in their basins. Pesticides with substantial use in both agricultural and nonagricultural applications—simazine, chlorpyrifos, malathion, diazinon, and carbaryl—had concentration trends that were mostly explained by a combination of agricultural-use trends and concentration trends in urban streams, which serve as a surrogate for trends in nonagricultural uses. The importance of the urban stream trends for explaining concentration trends in major rivers indicates the significance of nonagricultural uses of some pesticides to concentrations in major rivers, despite the much smaller area of urban land use compared to agriculture.

Streamflow (incorporated into the trend model) and trends in agricultural use of pesticides and urban use of pesticides (represented by concentration trends in Ryberg et al., 2010) are all important influences on pesticide concentration trends in streams and rivers. Consideration of these influences is vital to understanding trends in pesticide concentrations and, ultimately, to determining whether or not other factors, such as management practices, are also affecting concentration trends.

5. Disclosure statement

None of the authors have any actual or potential conflict of interest including any financial, personal, or other relationships with other people or organizations within three years of beginning the submitted work that could inappropriately influence, or be perceived to influence, their work.

Supplementary data

Supplementary material for this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2015.06.095.

Acknowledgments

The USGS National Water-Quality Assessment Program funded this work. The authors thank USGS personnel for collecting and analyzing stream-water samples and Nancy Baker (USGS) for geographic information system support. We also thank early reviewers Wes Stone and Lori Sprague (USGS) and anonymous reviewers for their constructive reviews.

References

Baker, N.T., Stone, W.W., 2013. Preliminary estimates of annual agricultural pesticide use for counties of the conterminous United States, 2010–11. U.S. Geological Survey Open-File Report 2013–1295 (2 pp. pamphlet, 14 tables, accessed February 3, 2014, at http://dx.doi.org/10.3133/ofr20131295).

Crawford, C.G., 2004. Sampling strategies for estimating acute and chronic exposures of pesticides in streams. J. Am. Water Resour. Assoc. 40 (2), 485–502.

Donaldson, D., Kiely, T., Grube, A., 2002. Pesticides industry sales and usage — 1998 and 1999 market estimates: Biological and Economic Analysis Division, Office of Pesticide Programs. Office of Prevention, Pesticides, and Toxic Substances. U.S. Environmental Protection Agency Pesticides Industry Sales and Usage Report (33 p., accessed January 6, 2015, at http://www.epa.gov/pesticides/pestsales/99pestsales/market_estimates1999.pdf).

Edwards, T.K., Glysson, G.D., 1999. Field methods for measurement of fluvial sediment. U.S. Geological Survey Techniques of Water-Resources Investigations book 3, chapter C2, (89 pp., http://pubs.er.usgs.gov/usgspubs/twri/twri03C2).

Fry, J., Xian, G., Jin, S., Dewitz, J., Homer, C., Yang, L., Barnes, C., Herold, N., Wickham, J., 2011. Completion of the 2006 National Land Cover Database for the Conterminous United States. PE&RS 77 (9), 858–864 (accessed June 16, 2015, at http://www.mrlc.gov/downloadfile2.php?file=September2011PERS.pdf).

Gilliom, R.J., Alley, W.M., Gurtz, M.E., 1995. Design of the National Water-Quality Assessment Program—occurrence and distribution of water-quality conditions. U.S. Geological Survey Circular 1112 (33 pp., http://water.usgs.gov/pubs/circ/circ1112/).

Gilliom, R.J., Barbash, J.E., Crawford, C.G., Hamilton, P.A., Martin, J.D., Nakagaki, Naomi, Nowell, L.H., Scott, J.C., Stackelberg, P.E., Thelin, G.P., Wolock, D.M., 2006. The quality of our Nation's waters—pesticides in the Nation's streams and ground water, 1992–2001. U.S. Geological Survey Circular 1291 (172 pp.).

Grube, A., Donaldson, D., Kiely, T., Wu, L., 2011. Pesticides industry sales and usage—2006 and 2007 market estimates. U.S. Environmental Protection Agency Pesticide Industry Sales and Usage Report EPA 733-R-11-001 (33 pp., accessed June 17, 2015, at http://www.epa.gov/opp00001/pestsales/07pestsales/table_of_contents2007.htm).

Lindley, C.E., Stewart, J.T., Sandstrom, M.W., 1996. Determination of low concentrations of acetochlor in water by automated solid-phase extraction and gas chromatography with mass-selective detection. J. AOAC Int. 79 (4), 962–966.

Madsen, J.E., Sandstrom, M.W., Zaugg, S.D., 2003. Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—a method supplement for the determination of fipronil and degradates in water by gas chromatography/mass spectrometry. U.S. Geological Survey Open-File Report 02-462 (11 pp., http://nwql.usgs.gov/Public/pubs/OFR02-462/OFR02-462.html).

Martin, J.D., Eberle, Michael, 2011. Adjustment of pesticide concentrations for temporal changes in analytical recovery, 1992–2010. U.S. Geological Survey Data Series 630 (11 pp., 5 app., http://pubs.usgs.gov/ds/630/).

Martin, J.D., Eberle, Michael, Nakagaki, Naomi, 2011. Sources and preparation of data for assessing trends in concentrations of pesticides in streams of the United States, 1992–2010. U.S. Geological Survey Data Series 655 (23 pp., 5 app., http://pubs.usgs.gov/ds/655/).

Neter, J., Kutner, M.H., Nachtsheim, C.J., Wasserman, W., 1996. Applied Linear Statistical Models. 4th ed. WCB/McGraw-Hill, Boston, Mass. (1,408 pp.).

Ryberg, K.R., Vecchia, A.V., 2012. waterData—an R Package for retrieval, analysis, and anomaly calculation of daily water data, version 1.0. U.S. Geological Survey Open-File Report 2012–1168 (8 pp., accessed October 12, 2012, at http://pubs.usgs.gov/of/2012/1168/).

Ryberg, K.R., Vecchia, A.V., 2013. seawaveQ—an R package providing a model and utilities for analyzing trends in chemical concentrations in streams with a seasonal wave (seawave) and adjustment for streamflow (Q) and other ancillary variables. U.S. Geological Survey Open-File Report 2013–1255 (13 pp., with 3 appendixes, accessed December 30, 2013, at http://dx.doi.org/10.3133/ofr20131255).

Ryberg, K.R., Vecchia, A.V., Martin, J.D., Gilliom, R.J., 2010. Trends in pesticide concentrations in urban streams in the United States, 1992–2008. U.S. Geological Survey Scientific Investigations Report 2010–5139 (101 pp., http://pubs.usgs.gov/sir/2010/5139/).

Ryberg, K.R., Vecchia, A.V., Gilliom, R.J., Martin, J.D., 2014. Pesticide trends in major rivers of the United States, 1992–2010. U.S. Geological Survey Scientific Investigations Report 2014–5135 (63 pp., http://dx.doi.org/10.3133/sir20145135).

Shelton, L.R., 1994. Field guide for collecting and processing stream-water samples for the National Water-Quality Assessment Program. U.S. Geological Survey Open-File Report 94–455 (42 pp.).

Stone, W.W., 2013. Estimated annual agricultural pesticide use for counties of the conterminous United States, 1992–2009. U.S. Geological Survey Data Series 752 (1 p. pamphlet, 14 tables, accessed July 22, 2013, at http://pubs.usgs.gov/ds/752/).

Stone, W.W., Gilliom, R.J., Ryberg, K.R., 2014. Pesticides in U.S. streams and rivers — occurrence and trends during 1992–2011. Environ. Sci. Technol. 48 (19), 11,025–11,030. http://dx.doi.org/10.1021/es5025367.

Sullivan, D.J., Vecchia, A.V., Lorenz, D.L., Gilliom, R.J., Martin, J.D., 2009. Trends in pesticide concentrations in corn-belt streams, 1996–2006. U.S. Geological Survey Scientific Investigations Report 2009–5132 (75 pp., http://pubs.usgs.gov/sir/2009/5132/).

Thelin, G.P., Stone, W.W., 2013. Estimation of annual agricultural pesticide use for counties of the conterminous United States, 1992–2009. U.S. Geological Survey Scientific Investigations Report 2013–5009 (54 pp., accessed July 22, 2013, at http://pubs.usgs.gov/sir/2013/5009/).

Therneau, T.M., 2013. survival—a package for survival analysis in S: R package version 2.37-4. (accessed July 22, 2013, at http://CRAN.R-project.org/package=survival).

U.S. Department of Agriculture National Agricultural Statistics Service, 2014. National statistics for corn. (accessed September 15, 2014, at http://quickstats.nass.usda.gov/results/08638011-B478-3942-B44F-FA130ADDE283?pivot=short_desc).

U.S. Environmental Protection Agency, 2000. Status of chemicals in special review: EPA-738-R-00-001. (59 pp., accessed June 17, 2015, at http://www.epa.gov/oppsrrd1/docs/sr00status.pdf).

U.S. Environmental Protection Agency, 2002. Interim Reregistration eligibility decision for Chlorpyrifos: EPA 738-R-01-007. (259 pp., accessed June 17, 2015, at http://nepis.epa.gov/Exe/ZyPDF.cgi/200008BM.PDF?Dockey=200008BM.PDF).

U.S. Environmental Protection Agency, 2004. Carbaryl IRED facts. US Environmental Protection Agency Office of Pesticide Programs Fact Sheet (6 pp., accessed January 6, 2015, at http://www.epa.gov/pesticides/reregistration/REDs/factsheets/carbaryl_factsheet.pdf).

U.S. Environmental Protection Agency, 2006a. Decision documents for atrazine. (323 pp., accessed June 16, 2015, at http://www.epa.gov/pesticides/reregistration/REDs/atrazine_combined_docs.pdf).

U.S. Environmental Protection Agency, 2006b. Reregistration eligibility decision for diazinon: EPA 738-R-04-006. (112 pp., accessed June 16, 2015, at http://www.epa.gov/pesticides/reregistration/REDs/diazinon_red.pdf).

U.S. Environmental Protection Agency, 2006c. Reregistration eligibility decision for simazine: EPA 738-R-06-008. (266 pp., accessed June 17, 2015, at http://www.epa.gov/pesticides/reregistration/REDs/simazine_red.pdf).

U.S. Environmental Protection Agency, 2007a. Reregistration eligibility decision (RED) for carbaryl. (accessed June 16, 2015, at http://www.epa.gov/pesticides/reregistration/REDs/carbaryl_red.pdf).

U.S. Environmental Protection Agency, 2007b. Reregistration eligibility decision for carbofuran: EPA-HQ-OPP-2005-0162. ([variously paged], accessed June 17, 2015, at http://www.epa.gov/oppsrrd1/reregistration/REDs/carbofuran_red.pdf).

U.S. Environmental Protection Agency, 2008a. Amended reregistration eligibility decision (RED) for carbaryl. (43 pp., accessed June 16, 2015, at http://www.epa.gov/pesticides/reregistration/REDs/carbaryl-red-amended.pdf).

U.S. Environmental Protection Agency, 2008b. Diazinon—phase out of all residential uses of the insecticide. (accessed June 17, 2015, at http://www.epa.gov/opp00001/factsheets/chemicals/diazinon-factsheet.htm).

U.S. Environmental Protection Agency, 2009. EPA 816-F-09-004. National Primary Drinking Water Regulations (6 pp., accessed June 16, 2015, at http://www.epa.gov/ogwdw/consumer/pdf/mcl.pdf).

U.S. Geological Survey, variously dated, National field manual for the collection of water-quality data: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chaps. A1–A9, http://water.usgs.gov/owq/FieldManual

Vecchia, A.V., 2003. Relation between climate variability and stream water quality in the continental United States. Hydrol. Sci. Technol. 19 (1), 77–98.

Vecchia, A.V., Martin, J.D., Gilliom, R.J., 2008. Modeling variability and trends in pesticide concentrations in streams. J. Am. Water Resour. Assoc. 44 (5), 1,308–1,324.

Vecchia, A.V., Gilliom, R.J., Sullivan, D.J., Lorenz, D.L., Martin, J.D., 2009. Trends in concentrations and use of agricultural herbicides for Corn Belt rivers, 1996–2006. Environ. Sci. Technol. 43, 9,096–9,102.

Zaugg, S.D., Sandstrom, M.W., Smith, S.G., Fehlberg, K.M., 1995. Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—determination of pesticides in water by C-18 solid-phase extraction and capillary-column gas chromatography/mass spectrometry with selected-ion monitoring. U.S. Geological Survey Open-File Reportpp. 95–181 (49 pp.).